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COMPLETE SPECIFICATION

Improvements in or relating to Resins

We, HERCULES POWDER COMPANY, a corporation organised under the laws of the State of Delaware, one of the United States of America, of 900 Market Street, City of Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the manufacture of novel condensation products obtained by reacting a polyamide derived from a polyalkylene polyamine and a saturated aliphatic dibasic carboxylic acid containing from 3—10 carbon atoms with epichlorohydrin alone or in conjunction with a quaternizing agent. These novel condensation products range from water-soluble cationic thermosetting resins which are useful in a variety of applications to condensation products that can be converted easily to water-soluble cationic thermosetting resins by further condensation. The invention includes the novel condensation products, methods of preparing the products and various applications thereof.

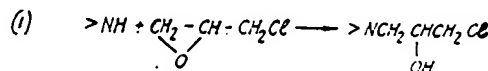
In the preparation of these products, the dibasic carboxylic acid is first reacted with

the polyalkylene polyamine under conditions such as to produce a water-soluble polyamide containing the recurring groups



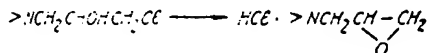
where n and x are each 2 or more and R is the divalent hydrocarbon radical of the dibasic carboxylic acid. This long chain polyamide is then reacted with epichlorohydrin and optionally with a quaternizing agent to form the water-soluble condensation products of the invention.

The reaction between the epichlorohydrin and the long chain polyamide is believed to take place in three stages, the first involving reaction of the epichlorohydrin with the secondary amine groups of the polyamide in accordance with the following equation in which >NH represents the secondary amine groups:

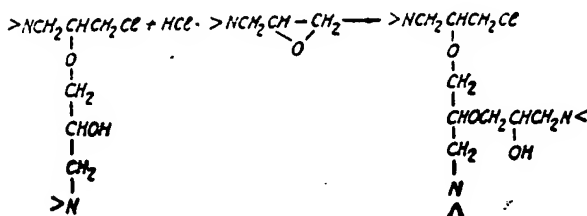
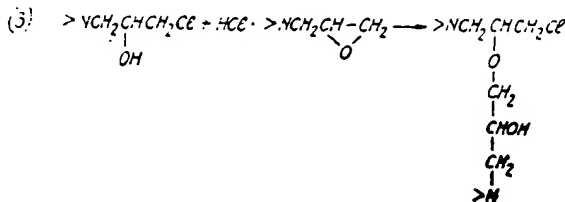


the second involving reaction of the chlorohydrin groups in accordance with the following equation:

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and the third involving cross-polymerization and the formation of a cationic resin which may occur through the following reactions:



or may involve reaction between chloride of the chlorohydrin groups and tertiary amine to form quaternary ammonium compounds. These reactions, as well as others, may occur simultaneously.

The polyamides utilized in preparing the condensation products of the present invention are obtained by reacting a saturated aliphatic dibasic carboxylic acid containing from 3 to 10 carbon atoms, such as malonic, succinic, adipic or azelaic acid, with a polyalkylene polyamine containing from 2 to 8 alkylene groups, preferably in aqueous solution. The saturated dibasic acids having from 4 to 8 carbon atoms in the molecule are preferred. Blends of two or more of the saturated dibasic carboxylic acids may also be used.

A variety of polyalkylene polyamines including polyethylene polyamines, polypropylene polyamines and polybutylene polyamines, may be employed herein of which the polyethylene polyamines represent an economically preferred class. More specifically, the polyalkylene polyamines of this invention may be represented as polyamines in which the nitrogen atoms are linked together by groups of the formula $-C_nH_{2n}-$ where n is a smaller integer greater than unity and the number of such groups in the molecule ranges from two up to eight. The nitrogen atoms may be attached to adjacent carbon atoms in the group $-C_nH_{2n}-$ or to carbon atoms further apart, but not to the same carbon atom. This invention contemplates not only the use of such polyamines as diethylenetriamine, triethylenetetramine, tetraethylenepentamine, dipropyl-

amine, which can be obtained in reasonably pure form, but also mixtures and various crude polyamine materials. For example, the mixture of polyethylene polyamines obtained by the reaction of ammonia and ethylene dichloride, refined only to the extent of removal of chlorides, water, excess ammonia, and ethylenediamine, is a very satisfactory starting material. Products prepared from a distillation residue from the refining of the lower polyethylene polyamines and consisting largely of polyamines higher than tetraethylenepentamine may also be used. It is also to be understood that compounds containing small groups attached to nitrogen, such as $-CH_2CH_2OH$, which are nearly always present to some extent in commercial polyamines as a result of a side reaction in the usual process by which the polyalkylene polyamines are manufactured, are also included within the scope of this invention. We may also use hydroxyalkyl substituted polyamines. The term "polyalkylene polyamine" employed in the claims, therefore, refers to and includes any of the polyalkylene polyamines referred to above or to a mixture of such polyalkylene polyamines.

It is desirable, in some cases, to increase the spacing of secondary amino groups on the polyamide molecule in order to change the reactivity of the polyamide-epichlorohydrin complex. This can be accomplished by substituting a diamine such as ethylenediamine, propylenediamine, hexamethylenediamine and the like for a portion of the polyalkylene polyamine. For this purpose, up to about 80% by weight of the polyalkylene polyamine may be replaced by a molecularly equivalent amount of the diamine.

Usually, a replacement of about 50% by weight or less will serve the purpose.

The temperatures employed for carrying out the reaction between the dibasic acid and the polyalkylene polyamine may vary from about 110° C. to about 250° C. or higher at atmospheric pressure. For most purposes, however, temperatures between about 160° C. and 210° C. have been found satisfactory and are preferred. Where reduced pressures are employed somewhat lower temperatures may be utilized. The time of reaction depends on the temperatures and pressures utilized and will ordinarily vary from about $\frac{1}{2}$ to 2 hours, although shorter or longer reaction times may be utilized depending on reaction conditions. In any event, the reaction is desirably continued to substantial completion for best results.

In carrying out the reaction, it is preferred to use an amount of dibasic acid sufficient to react substantially completely with the primary amine groups of the polyalkylene polyamine but insufficient to react with the secondary amine groups to any substantial extent. This will usually require a mole ratio of polyalkylene polyamine to dibasic acid of from about 0.9:1 to about 1.2:1. However, mole ratios of from about 0.8:1 to about 1.4:1 may be used with quite satisfactory results. Mole ratios outside of these ranges are generally unsatisfactory. Thus, mole ratios below about 0.8:1 result in a gelled product or one having a pronounced tendency to gel while mole ratios above 1.4:1 result in low molecular weight polyamides.

The polyamide, formed as above described, may be converted to a cationic thermosetting resin by reacting it with epichlorohydrin at a temperature from about 45° C. to about 100° C. and preferably between about 45° C. and 70° C. until the viscosity of a 20% solids solution at 25° C. has reached about C or higher in the Gardner-Holdt Scale. This reaction is preferably carried out in aqueous solution to moderate the reaction. pH adjustment is usually not necessary. However, since the pH decreases during the polymerization phase of the reaction it may be desirable, in some cases, to add alkali to combine with at least some of the acid formed. This will create an environment favoring the conversion of the chlorohydrin groups to epoxide groups, thereby increasing the ratio of the latter to the former.

When the desired viscosity is reached, sufficient water is then added to adjust the solid content of the resin solution to about 10% or less, the product cooled to about 25° C. and then stabilized by adding sufficient acid to reduce the pH at least to about 6 and preferably to at least about 5. Any suitable acid such as hydrochloric, sulfuric, nitric, formic, phosphoric and acetic acid

may be used to stabilize the product. However, hydrochloric acid is preferred.

In the polyamide—epichlorohydrin reaction, it is preferred to use sufficient epichlorohydrin to convert all secondary amine groups to tertiary amine groups. However, more or less may be added to moderate or increase reaction rates. In general, satisfactory results may be obtained utilizing from 0.5 moles to 1.8 moles of epichlorohydrin for each secondary amine group of the polyamide. It is preferred to utilize from about 1.0 mole to about 1.5 moles for each secondary amine group of the polyamide.

The polyamide—epichlorohydrin resins prepared as above described are highly efficient for use as wet-strength resins for paper and in many other applications to be described in more detail hereinafter. Such resins, however, are relatively unstable in aqueous solutions at higher solids concentrations so that the costs of handling, shipping and storing are somewhat high. If desired, the stability of these resins may be improved by incorporating into the resin formulation appropriate amounts of an agent capable of quaternizing tertiary nitrogen atoms formed by reaction of the epichlorohydrin with secondary amino groups of the polyamide. The resulting resins are stable for relatively long periods of time at total solids of 25% and higher and appear to retain all of the desirable features of the less stable resins.

In the preparation of these more stable polyamide—epichlorohydrin resins, a polyamide, prepared as previously described, is reacted with epichlorohydrin and a quaternizing agent, the conditions of reaction and the reactants, except for the inclusion of the quaternizing agent, being essentially the same as previously described. In a preferred procedure, the epichlorohydrin is first added to an aqueous solution of the polyamide at a temperature from about 45° to 55° C. The reaction mixture is then heated at a temperature from about 50° to 100° C. and preferably from about 60° to 80° C. depending upon the rate of polymerization desired. After a suitable time at this temperature, i.e., from about 0—100 minutes, and preferably until the viscosity of an approximately 25% solids solution of the reaction mixture at 25° C. is from about <A to <B on the Gardner-Holdt scale, at which time most of the epoxy groups of the epichlorohydrin have reacted with the secondary amine groups of the polyamide, the quaternizing agent is added and the reaction mixture heated, preferably at a temperature from about 60° C. to about 80° C., until the viscosity of an approximately 25% solids solution at 25° C. is at least A and preferably at least B on the Gardner-Holdt scale. The solids-viscosity relation-

ship may be obtained by (1) direct polymerization at the 25% level, (2) polymerization at a higher level followed by dilution to 25% solids, or (3) polymerization at a lower level followed by concentration at less than 40° C. and under reduced pressure to 25% solids. The pH of the reaction mixture is then reduced to about 4.0 and preferably to about 2.0 to 3.0 with any suitable acid such as sulfuric, hydrochloric, formic and the like. The initial degree of polymerization, quantity of quaternizing agent and final pH are all important in controlling the stability of the resins.

The amount of quaternizing agent utilized should be sufficient to convert from about 25% to about 75%, and preferably about 50% of the tertiary amine groups to quaternary groups. The amount of epichlorohydrin utilized will be the same as before.

The quaternizing agent may be any compound capable of quaternizing a tertiary nitrogen atom in an aqueous medium. In general, these compounds are characterized by having as a principal part of their structure an alkyl group or substituted alkyl group which is readily available for alkylation under the conditions herein described. These include the lower alkyl esters of mineral acids such as the halides, sulfates and phosphates and substituted alkyl halides. Illustrative of the compounds which may be used are dimethyl, diethyl and dipropyl sulfate, methyl chloride, methyl iodide, methyl bromide, ethyl bromide, propyl bromide, the mono-, di- or tri-methyl, ethyl and propyl phosphates, 1,3-dichloro-propanol-2 and 1-chloroglycerol. Certain aromatic compounds may also be used. Typical of these are benzyl chloride and methyl p-toluene sulfonate.

The invention also contemplates the preparation of water-soluble condensates of epichlorohydrin and a polyamide of the type hereinabove described which, while they are not per se useful as wet-strength resins and so on, may be converted readily to such by further condensation. These condensates are quite stable at solids concentrations up to about 40% or more so that savings both in transportation and storage costs may be realized by virtue of the decreased bulk and weight of this higher solids content material.

In the preparation of these condensates the polyamide, formed as above described, is reacted with epichlorohydrin, the amounts of reactants and conditions of reaction being the same as previously described, except, that in this case, the reaction is terminated upon completion of reaction (1) described hereinabove and before any substantial amount of cross-linking takes place. In practice, this result can be satisfactorily obtained by terminating the reaction before the viscosity of a 35—40% solids solution of the condensate reaches C on the Gardner-Holdt

scale. It is preferred to terminate the reaction when the viscosity of a 35—40% solids solution of the condensation product is between A and B on the Gardner-Holdt scale.

When the desired viscosity is reached, which will usually require heating for a period of time from about 2 minutes to about 15 minutes within the temperature range previously indicated, the reaction is terminated immediately. This may be accomplished effectively by adding sufficient acid to reduce the pH to 7 and then cooling the mixture rapidly to 25° C. The mixture is then stabilized, as before, by adding sufficient acid to reduce the pH preferably at least to about 5.

The water-soluble condensates, prepared as above described, may be converted readily to cationic thermosetting resins by diluting to about 20% by weight solids, adding sufficient alkali, i.e., sodium carbonate or sodium hydroxide, to adjust the pH to from about 10.5 to 12.0, and then allowing the solution to stand at room temperature until the viscosity has increased to about D or higher on the Gardner-Holdt scale. This will usually require about 4 hours, more or less, depending on the particular pH used. Thus, the higher the pH, the more rapid will be the increase in viscosity.

When the desired viscosity is reached, the resin is diluted to about 10% solids or less and, if not used immediately, is stabilized, as before, by the addition of sufficient acid to reduce the pH preferably at least to about 5.

The cationic resins, formed in accordance with the procedures hereinabove described, are useful in a number of applications. One of these is in the wet-strengthening of paper, paper-board and similar fibrous products made from cellulose fibers. Thus, it has been found that a high degree of wet-strength is imparted to paper and paper products when these resins are incorporated therein or applied thereto in amounts ranging from about 0.1% to about 5% (resin solids based on dry weight of paper). The resins may be applied by tub application or by spraying, if desired. Thus, for example, preformed and partially or completely dried paper may be impregnated by immersion in, or spraying with, an aqueous solution of the resin following which the paper may be heated for about 0.5 to 30 minutes at temperatures of 90° C. to 100° C. or higher to dry same and cure the resin to a water-insoluble condition. The resulting paper has greatly increased wet strength, and, therefore, this method is well suited for the impregnation of paper towels and absorbent tissue, as well as heavier stocks such as wrapping paper and bag paper, to impart wet strength characteristics thereto.

The preferred method of incorporating these resins in paper, however, is by internal addition prior to sheet formation whereby

advantage is taken of the substantivity of the resins for hydrated cellulosic fibers. In practicing this method, an aqueous solution of the resin in its uncured and hydrophilic state is added to an aqueous suspension of paper stock in the beater, stock chest, Jordan engine, fan pump, head box or at any other suitable point ahead of sheet formation. The sheet is then formed and dried in the usual manner, thereby curing the resin in its polymerized and water-insoluble condition and imparting wet strength to the paper.

The uncured cationic thermosetting resins of the invention, incorporated in paper in any suitable manner, as described above, may be cured under acid, neutral or alkaline conditions, i.e., at pH's from about 4.0 to 10, by subjecting the paper to a heat-treatment for about 0.5 to 30 minutes at a temperature from about 90 to 100° C. Optimum results, however, are obtained under alkaline conditions. In view of this, and the rather extensive corrosion of equipment encountered at pH's below about 6.0, it is preferred to carry out the curing step at a pH from about 6.0 to about 9.0.

The cationic resins of the invention are also useful as insolubilizing agents in the preparation of new and improved water-insoluble polymers from water-soluble polymers. In this application, a mixture of the cationic resin and water-soluble polymer is prepared and the mixture then dried either at room temperature or at elevated temperatures. In some instances, drying at an elevated temperature will give a somewhat more insoluble product and in such cases the higher temperature is preferred if a product of lower solubility in water is desired. Temperatures higher than 105° C. shown in the examples hereinafter given are applicable provided one does not reach the char temperature of the composition which will vary with the pH and type of polymer involved.

These products may be prepared over a wide pH range, i.e., from about 1.5 to 12. However, a pH range of 6 to 8 is preferred in most cases. The pH range desired will depend in part on the use to be made of the product.

The relative amounts of ingredients used in this application should be such as to give the desired insolubility to the product. Amounts of resin within the range of 2% to 175% by weight of the polymer have been used to give products having substantially higher insolubility than the starting materials. While amounts of resin lower than 2% can be used to give a product having somewhat higher insolubility than the starting materials, in most cases the water-insolubility of the product will not be as high as desired. In most cases the preferred amount of resin is from about 5% to 30% by weight of the polymer.

The initial concentration of the water-soluble polymer employed is immaterial, except insofar as it is desirable from a practical standpoint to have a polymer solution of such concentration that it may be readily mixed with the resin and also to have a mixture which is most suitable for film casting or other uses.

The insolubilizing process described above is applicable to modifying water-soluble polymers, and by the term "water-soluble polymers" we mean those which contain either carboxyl, hydroxyl, amine or amide groups or any combinations of said groups. Typical examples of such water-soluble polymers include the following: cellulose derivatives, e.g., carboxyalkyl celluloses such as carboxymethylcellulose, hydroxyalkyl celluloses such as hydroxyethyl cellulose, carboxyalkyl hydroxyalkyl celluloses such as carboxymethyl hydroxyethyl cellulose, sulfoalkyl celluloses such as sulfoethyl cellulose, alkyl celluloses such as methyl cellulose, alkyl hydroxyalkyl celluloses such as ethyl hydroxyethyl cellulose, alkylene celluloses such as allyl cellulose, alkylene alkyl celluloses such as allyl ethyl cellulose, and various other substituted celluloses, either in the free acid form or water-soluble salts thereof such as alkali metal and ammonium salts; starches, e.g., potato starch, wheat starch and corn starch; starch derivatives, e.g., carboxymethylated starch, hydroxyethylated starch and oxidized starches; gums, e.g., algin, guar gum, locust bean gum, gum tragacanth, gum arabic, agar psyllium seed, Irish moss, and water-soluble salts thereof such as alkali metal and ammonium salts; proteins such as casein, gelatin, animal glue, and soybean protein; synthetic polymers, e.g., poly(vinyl alcohol), polyacrylic acid and substituted polyacrylic acid such as polymethacrylic acid, water-soluble copolymers derived from maleic anhydride such as maleic anhydride-styrene copolymers, and water-soluble salts thereof such as alkali metal and ammonium salts; polyamides such as polyacrylamide; and polymeric amines such as polyvinylamine and polyethylene imine.

The use of the water-soluble cationic resins of the invention for insolubilizing water-soluble polymers has many advantages. Thus, water-soluble polymers may be insolubilized to a remarkable degree merely by air-drying an aqueous solution thereof containing the resin at room temperature over a wide range of pH. Without any additional treatment, with carboxymethylcellulose, for example, the product is highly resistant to water, acid, and organic solvents; films made from the product have excellent physical properties such as clarity, flexibility and strength, whereas prior are methods require high temperatures and acid conditions for curing and the resulting films have poor flexibility as well as low tensile strength and

elongation properties.

The cationic resins of the invention may also be used advantageously in processes for applying water-soluble and water-insoluble coating or impregnating materials to fibrous organic and inorganic materials such as paper fibers, textile fibers and glass fibers, which are then subsequently transformed into felted products, for example paper. It is particularly advantageous to use these resins in processes involving the internal addition of coating or impregnating materials to paper and the like wherein such materials are added to an aqueous pulp suspension, as in the beater or fan pump of a papermaking system, and the fibers then formed into sheets or webs and dried in the conventional manner.

For example, in an aqueous system containing fibrous cellulosic material of the type of paper pulp suspended therein together with from about 0.25% by weight to about 10% by weight of a water-soluble carboxyl-containing compound, the presence of relatively small amounts, i.e., from about 0.1% to about 5%, based on the dry weight of fiber, of these resins not only improves flocculation and deposition of the water-soluble carboxyl-containing compound on the fibers but also serves to anchor it to the fibers by the formation of a direct bond between the cationic resin and the water-soluble carboxyl-containing compound and by the affinity of the cationic resin for the fiber. In the similar employment of these resins in like amounts in conjunction with water-insoluble coating or impregnating materials improved retention of such materials by the fibers is likewise obtained. Moreover, in each case, the resulting products have improved characteristics, i.e., improved wet and dry strengths.

The cationic resin and the coating or impregnating material are preferably added to the aqueous pulp suspension in the form of aqueous solutions or, in the case of water-insoluble coating or impregnating materials, in the form of an aqueous emulsion or dispersion. The order of addition of the cationic resin and the coating or impregnating material, while not critical, is important for the attainment of optimum results. Thus, in the case of water-soluble coating or impregnating materials optimum results, i.e., maximum increase in dry and wet strength, are obtained when the cationic resin is added to the aqueous pulp suspension first and thoroughly mixed therewith prior to the addition of the water-soluble coating or impregnating agent. In the case of water-insoluble coating or impregnating materials, the order of addition will largely depend on the amount of cationic resin utilized. Thus, when less than about 0.5 to about 0.6% of the cationic resin is used, best results are obtained when the water-insoluble coating or impregnating

agent is added first and mixed thoroughly with the pulp before the cationic resin is added. When more than 0.5 to about 0.6% resin is used it is better to add the resin first.

A wide variety of water-soluble and water-insoluble coating or impregnating agents may be applied advantageously utilizing the cationic resins of the invention. Thus, any water-soluble or water-dispersible carboxyl-containing compound may be so applied. By the term "water-soluble or water-dispersible carboxyl-containing compound" we mean polymers and copolymers of acrylic acid and methacrylic acid such as copolymers of acrylamide-acrylic acid, methacrylamide-acrylic acid, acrylonitrile-acrylic acid and methacrylonitrile-acrylic acid; copolymers involving one of several alkyl acrylates and acrylic acid, copolymers involving one of several alkyl methacrylates and acrylic acid, copolymers involving one of several alkyl vinyl ethers and acrylic acid; and similar copolymers in which methacrylic acid is substituted in place of acrylic acid in the above examples; water-soluble cellulose ethers such as carboxymethylcellulose and carboxymethyl hydroxyethyl cellulose, the alkali metal and ammonium salts of water-soluble cellulose ethers, the alkali metal salts of styrene-maleic anhydride copolymers, the alkali metal salts of rosin including wood rosin, gum rosin and tall oil rosin, the alkali metal salts of modified rosin such as disproportionated rosin, polymerized rosin and partially hydrogenated rosin, the alkali metal salts of adducts of rosin with materials such as maleic acid, fumaric acid and itaconic acid as well as the anhydrides of these acids, and the alkali metal salts of various saturated and/or unsaturated fatty acids containing from about 10 to about 22 carbon atoms.

Exemplary of the acrylic type polymers and copolymers with which the resins of the invention may be utilized are those described in United States Patent Specification No. 2,661,309 and Canadian Patent Specification No. 547,577.

The water-soluble or water-dispersible compounds with which the resins herein described may be utilized to advantage also include condensates of lower alkylene oxides with polymers of acrylic acid, methacrylic acid and itaconic acid having average molecular weights above about 1000 and condensates of lower alkylene oxides with copolymers of acrylic acid, methacrylic acid and itaconic acid containing at least about 35 mole per cent, and preferably at least about 50 mole per cent, of one or more of these acids as the substituent monomer units. Polymerizable compounds which may be copolymerized with one or more of these acids or with salts of such acids include esters of acrylic acid, methacrylic acid, itaconic acid,

maleic acid, fumaric acid and citraconic acid and monohydric alcohols such as methyl, butyl, octyl, dodecyl and cyclohexyl alcohols; vinyl and vinyloxyalkyl esters of carboxylic acids such as acetic and propionic esters; vinyl ethers such as ethyl vinyl ether and butyl vinyl ether; acrylamide; and methacrylamide. Preparation of these carboxylic-containing polymers and copolymers and the condensation of same with alkylene oxides may be carried out by well-known procedures. In the latter reaction, the proportion of alkylene oxide introduced may vary from about 1 mole per cent to 250 mole per cent, and preferably from about 10 mole per cent to about 95 mole per cent of the carboxylic-containing units of the polymer.

The water-insoluble coating or impregnating materials which may be applied advantageously utilizing the cationic resins of the invention include materials such as resins, precipitated or insoluble sizes, elastomers, waxes, pitches, bitumens and oils, as well as the various clays and/or pigments utilized in the manufacture of filled or coated papers. Typical water-insoluble materials of this type which may be so applied are disclosed in United States Patent Specification No. 2,601,598. The cationic resins of the invention may also be used to advantage in the application of ketene dimers to paper. These, in some cases, may be dispersed directly in the aqueous pulp suspension. They also may be utilized in the form of aqueous emulsions such as those disclosed in United States Patent Specification No. 2,627,477, or in any other suitable manner such as in the form of aqueous dispersions of ketene dimer compositions comprising ketone dimer supported on particles of a finely-divided inorganic material such as clay or silica. Ketene dimer compositions of the latter type are disclosed in our British Patent Specification No. 830,099. In addition, these resins may be used advantageously to apply nonionic and anionic wax emulsions.

Another application in which the cationic resins of the invention may be used to advantage is in the preparation of fibrous sheets, mats and other fibrous products from mineral fibers such as glass, mineral wool and asbestos fibers. Thus, it has been found that the incorporation of the resin in mineral fiber sheets and mats in amounts from about 0.4% to about 12% (resin solids based on weight of fiber) improves interfiber bonding and imparts wet-strength to these products. In the preparation of such products an aqueous solution of the resin may be added to an aqueous suspension of the fibers and the fibers then formed into sheets or mats and dried in a conventional manner. Alternatively, an aqueous solution of the resin may be applied to a preformed and partially or completely dried sheet or mat by spraying,

immersion and so on and the sheet or mat then dried in any convenient manner such as by air drying, drying on heated rolls, in heated tunnels, by means of infrared lamps or in ovens.

The cationic resins of the invention are also useful for preventing shrinkage and felting of wool. Thus, it has been found that when a wool fabric is treated with from about 0.5% to about 10% by weight, based on the dry weight of fabric, of the cationic resin shrinkage and felting of the fabric are substantially prevented. This treatment, moreover, does not add harshness or stiffness to the fabric and does not significantly yellow or otherwise change the color of the fabric.

In this application, an aqueous solution of the resin is applied to the fabric in any suitable manner as by dipping, spraying, padding or the like and the fabric then dried in any suitable manner. This treatment may be carried out under acid, neutral or alkaline conditions, i.e., at pH's from about 3 to about 10 and preferably from about 5 to about 8. The treatment is applicable to wool fabrics prepared from animal hair such as sheep wool, mohair, cashmere, camel hair, alpaca wool, vicuna wool and llama wool as well as blends of animal hair with natural and/or synthetic fibers such as cotton, polyacrylonitrile fiber, polyterephthalate ester fibers and polyamide fibers.

Still another useful application of the cationic resins of the invention is in the manufacture of nonwoven fabrics. Thus it has been found that a strongly bonded nonwoven fabric may be prepared by impregnating a dry fiber web with an aqueous solution of the resin and then drying the web. The resin may be used alone or in conjunction with any of the well-known synthetic latices such as nitrile rubber, styrene rubber, poly(vinyl chloride), poly(vinyl acetate), and polyacrylics as well as with natural rubber latex. When used alone, the cationic resins of the invention have a number of advantages over the solution binders of the prior art. Thus (1) they are supplied as low viscosity aqueous solutions, (2) film formation requires only loss of solvent (water), i.e., does not require high temperature curing conditions to form cohesive film strength or an adhesive bond and (3) does not require a catalyst or pH extremes to form bond. When used in conjunction with latex emulsions, an unexpected result is obtained in that there is an unexpected increase in both wet and dry strength. In other words, the use of the resin in conjunction with the latex emulsion gives greater wet and dry strength in the nonwoven fabric than can be achieved with either binder alone. It appears, therefore, that there is a synergistic effect when the two types of binders are used in combination.

In this application, textile fibers are first formed into fiber mats or webs in any suitable manner as by deposition from air or liquid or by conventional mechanical means such as carding. The fiber mats are then dried, if necessary, and impregnated, usually by spraying or dipping, with an aqueous solution of the cationic resin or a combination of the resin and suitable latex binders. The treated fabric is then dried at suitable temperatures, i.e., from about 75° C. to about 150° C. (preferably about 100° C.). Some pressure is required to get satisfactory bonding. This may be achieved in any suitable manner as, for example, with calender rolls.

When the cationic resin solution is used in conjunction with the latex emulsion the two may be mixed and then applied to the web. Alternatively, the web may be pretreated with the resin solution followed by treatment with the latex emulsion.

The amount of bonding material, i.e., resin alone or in combination with latex emulsion, to be applied will vary depending upon a number of factors such as the type of fiber, the particular bonding material and the results desired. In most cases, from about 5% by weight to about 20% by weight of bonding material (solids basis based on dry weight of fiber) will be satisfactory. While the resin and latex emulsion may be used in any desired proportion, it is preferred that the weight ratio of the former to the latter be from about 1:5 to about 1:1.

Still another useful application of the cationic resins of the invention is in the treatment of nonfibrous regenerated cellulose film to improve the bonding of said film to the subsequently applied top coat. In this application, an aqueous solution of the cationic resin may be applied to a nonfibrous regenerated cellulose film, as by dipping or spraying, and the treated film then dried by any of the commercially available methods of drying such as by passing it over hot rolls or through heated tunnels or by exposure to infrared lamps. Alternatively, since the cationic resin utilized herein is compatible with and soluble in a viscose solution, it may be incorporated in the film during manufacture thereof as by adding an aqueous solution of the resin to the viscose solution. After the film has been dried, a moisture-resistant top coat of any type conventionally used for this purpose is applied in the usual manner.

The amount of resin in or on the film will vary depending on the degree of anchoring desired and other factors. In some cases, as little as 1.0% by weight, based on the weight of the film, will suffice. In other cases, more or less may be desirable. In general, amounts above about 10.0% afford little, if any, added advantage and, hence,

will not ordinarily be used.

The resins herein disclosed are highly cationic and, when added to a viscose solution and the later then processed into film, are largely retained by the cellulose and carried through into the finished film. Some losses, however, are inevitable and allowance should be made for these when this procedure is utilized.

In the processing of unplasticized non-fibrous regenerated cellulose film, it is conventional practice to treat the film with glycerin or other polyol plasticizer commonly used for this purpose. The aqueous resin solutions of the present invention are compatible with such plasticizers in all proportions and, hence, the two may be mixed together and applied to, or incorporated in, the film in one step. Such resins, moreover, do not precipitate from the glycerol or like application bath in the presence of inorganic salts carried over from the acid regeneration bath.

The following examples are given to illustrate specific embodiments of the invention. Examples 1—23 illustrate the preparation of cationic resins in accordance with the invention and the use thereof for imparting wet strength to paper. The remaining examples illustrate other applications of the cationic resins of the invention.

EXAMPLE 1

Two hundred twenty-five grams (2.18 moles) of diethylenetriamine and 100 grams of water were placed in a 3-necked flask equipped with a mechanical stirrer, thermometer and condenser. To this was added 290 grams (2.0 moles) of adipic acid. After the acid had dissolved in the amine, the solution was heated to 185—200° C. and held there for 1½ hour. Then vacuum from a water pump was applied to the flask during the period required for the contents of the flask to cool to 140° C. following which 430 grams of H₂O was added. The polyamide contained 52.3% by weight solids and had an acid number of 2.1.

To 60 grams of this polyamide solution in a round-bottom flask was added 225 grams of H₂O. This solution was heated to 50° C. and 12.5 grams of epichlorohydrin was added dropwise over a period of 11 minutes. The contents of the flask was then heated to 60—70° C. until it had attained a Gardner viscosity of >E. Then 150 grams of H₂O was added to the product, and it was cooled to 25° C. Eleven ml. of 10% by weight HCl was then added to adjust the pH to 5.0. The product contained 9.0% by weight solids and had a Gardner viscosity of C—D.

Tacoma-bleached kraft was beaten to a Schopper-Reigler freeness of 750 cc. in a Noble and Wood cycle beater. The pulp was then adjusted to pH 9.0 with 10% by weight NaOH and 1.0% by weight, based

on the dry weight of pulp, of the polyamide—epichlorohydrin resin, prepared as described, was added. The pulp was sheeted in a Noble and Wood handsheet machine using a closed system in which the white water contained 100 p.p.m. sulfate ion and had been adjusted to pH 9.0 with 10% by weight NaO. A portion of the resulting handsheets were given an additional cure of 1 hour at 105° C. The sheets tested for wet strength were soaked for 2 hours in distilled water. Results are listed in Table I.

EXAMPLE 2

A polyamide was prepared from 319 grams (2.18 moles) of triethylenetetramine and 290 grams (2.0 moles) of adipic acid according to the procedure described in Example 1. The polyamide solution contained 49.8% by weight solids, and had a pH of 10.8 and an acid number of 3.2.

Sixty-three grams of the polyamide solution was dissolved in 225 grams of H₂O. This solution was stirred mechanically and heated to 50° C. Twenty-five grams of epichlorohydrin was added dropwise over a period of three minutes. The solution was then heated to 60–70° C. until it reached a viscosity of E (Gardner). Then it was diluted with 225 grams of H₂O, cooled to 25° C. and adjusted to pH 5.0 with 11 ml. of 10% by weight HCl. The product containing 8.4% by weight solids and having a Gardner viscosity of <C, was evaluated in bleached kraft pulp according to the procedure presented in Example 1. Results are listed in Table I.

EXAMPLE 3

Using the procedure outlined in Example 1, a polyamide was prepared from 88 grams (0.855 mole) of diethylene triamine, 29.5 grams (0.22 mole) of N-bis(aminopropyl) methylamine and 145 grams (0.99 mole) of adipic acid. Sixty grams of the polyamide

solution (52.8% by weight solids) was dissolved in 225 grams of H₂O and heated to 50° C. While this solution was being stirred 14 grams of epichlorohydrin was added dropwise over a period of 15 minutes. This solution was then heated to 60–70° C. until its viscosity equalled E on the Gardner scale (2 hours and 5 minutes). Then 175 grams of H₂O was added and the resin was cooled to 25° C. To this was added 13 ml. of 10% by weight HCl to adjust pH to 5.0. The product had a viscosity of B–C, Gardner, and contained 8.6% by weight solids. It was evaluated in paper as outlined under Example 1. Results are listed in Table I.

EXAMPLE 4

A polyamide was prepared according to the procedure given in Example 1 using 225 grams (2.18 moles) of diethylenetriamine and 218 grams (1.5 moles) of adipic acid and 94 grams (0.5 mole) of azelic acid. Fifty-seven and one half grams of the polyamide solution (55% by weight solids) was dissolved in 115 grams of H₂O and heated to 50° C. To this was added 15 grams of epichlorohydrin over a period of 6 minutes. This solution was then heated at 60–70° C. until the viscosity of the condensate reached >E (Gardner). Then 150 grams of H₂O was added and the product was cooled to 25° C. It was adjusted to pH 5.0 by adding 10 ml. of 10% by weight HCl. The finished resin had a viscosity of B (Gardner) and contained 9.5% by weight solids. It was evaluated in paper according to the procedure outlined in Example 1. Results are listed in Table I.

EXAMPLE 5

Sheets of paper were prepared and tested, as in Example 1, except that no resin was incorporated. The results are set forth in Table I.

TABLE I

Example	% (by weight) Resin Added Based on Dry Pulp	Basis Weight lb./3000 sq. ft.	Wet Tensile lb./in.	Wet Tensile Cured lb./in.
1	1.0	40.6	6.5	8.5
2	1.0	39.2	5.9	8.6
3	1.0	40.3	6.0	8.2
4	1.0	40.8	7.4	8.7
5	0.0	40.5	0.2	1.1

EXAMPLE 6

A polyamide was prepared from the following ingredients:

Diethylenetriamine	204.4 grams (1.98 moles)
Ethylenediamine	14.0 grams (0.24 moles)
Adipic acid	290.0 grams (1.98 moles)
Water	100.0 grams

The procedure of Example 1 was followed with the following exceptions. (1) The reaction mixture was held between 180° C. and 195° C. for 45 minutes; (2) aspirator vacuum was used during this entire period; and (3) the mixture was cooled to 140° C. and diluted with 430 ml. of distilled water (80° C.). The polyamide solution contained 52.4% by weight total solids and had an acid number of 3.4.

To 60.5 grams of this polyamide solution was added 225.0 grams of H₂O. This solution was heated to 50° C. and 11.25 grams of epichlorohydrin was added dropwise over a period of about 11 minutes. The solution was then heated to 70–80° C. and held at this temperature until it had attained a viscosity of E, Gardner-Holdt. It was then diluted with 173 ml. of water and adjusted to pH 5.0 with dilute HCl. The product contained 8.9% by weight solids and had a Gardner viscosity of B–C.

Tacoma bleached Kraft Waterleaf sheets were tubsized (30-second dip) in a 2.0% by weight solution of the resin, prepared as above described, and adjusted to pH 9.0 with 10% by weight sodium hydroxide. The sheets were squeezed (roll) and drum dried. Half were cured at 105° C. for one hour and the cured and uncured sheets then soaked in distilled water for 2 hours and tested for Mullen burst. The Mullen burst (pounds per square inch-average of five determinations) was 10.8 for the uncured sheets and 15.2 for the cured sheets as compared with a Mullen burst of less than 1 for sheets which had not been treated with the resin.

EXAMPLE 7

Into a 1-liter, 3-necked round-bottom flask fitted with mechanical stirrer, thermometer and distilling condenser was placed 200 g. (1.94 moles) of diethylenetriamine and 100 g. of water. The flask was flushed with nitrogen and kept under a nitrogen blanket throughout the reaction. To the well-stirred mixture was added, in 6 approximately equal portions, 290 g. (2.00 moles) of adipic acid. After the acid had dissolved in the

amine, the solution was heated to 190 ± 5° C. and held there for 1.5 hours. The reaction mixture was then cooled to 140° C. and diluted with 430.0 g. of water. The polyamide solution contained 54.6% by weight solids and had an intrinsic viscosity (2% by weight solution in 1 N ammonium chloride) of 0.116.

To 116 g. (63 g. dry basis) of this polyamide solution in a round-bottom flask equipped with mechanical stirrer and thermometer was added 210 g. of water. The solution was heated with stirring to 50° C. and 25.0 g. of epichlorohydrin was added during a period of 2 minutes. The solution was heated to 70° C. and, after 10 minutes at this temperature 17.0 g. of dimethyl sulfate was added dropwise over a period of 7 minutes. The solution was heated with stirring at 70° C. until a Gardner viscosity of <C was attained (4 hours 16 minutes). It was then cooled to 25° C. and adjusted to pH 4.0 with 3.1 ml. of 10% by weight sulfuric acid. The product contained 27.0% by weight solids and had a Gardner viscosity of >B at 25° C. (Brookfield viscosity 51.2 cps. at 25° C.). The product was stable to storage at 25 ± 2° C. for at least 75 days. It was evaluated in paper as follows:

Tacoma bleached kraft pulp was beaten to a Schopper-Reigler freeness of 750 cc. in a Noble and Wood cycle beater. The pH of the pulp was 7.5–7.8. To this pulp was added 1.0% by weight of the polyamide—epichlorohydrin—dimethyl sulfate resin based on the dry weight of the pulp. The pulp was heated on a Noble and Wood handsheet machine using a closed system. The white water contained 200 p.p.m. sulfate ion and had been adjusted to pH 7.5 with sodium bicarbonate solution. The resulting handsheets were run through press rolls and then drum dried according to the usual procedure. Portions of the resulting handsheets were cured for 1 hour at 105° C. The sheets tested for wet strength were soaked for 2 hours in distilled water. Results are listed in Table II.

EXAMPLE 8

A polyamide prepared according to the procedure outlined in Example 7 was converted to a useful wet-strength resin as follows:

- 5 To a solution of 63.0 g. (dry basis) of the polyamide in 185.0 g. of water heated to 50° C. was added with stirring 31.0 g. of epichlorohydrin over a period of 3 minutes.
- 10 The temperature of the solution was then raised to 70° C. After 10 minutes at 70° C. 17.0 g. of dimethyl sulfate was added during a period of 5 minutes. The mixture was heated with stirring at 70° C. until its
- 15 viscosity at 25° C. reached <E on the Gardner scale (3 hours and 38 minutes). It was then diluted with 195.0 g. of water and held at 70° C. until its viscosity at 25° C. reached C on the Gardner scale (5 hours and
- 20 42 minutes). The solution was cooled to 25° C., adjusted to pH 4.0 with 0.8 ml. of 10% by weight sulfuric acid and concentrated by heating at 25° C. to 40° C. at reduced pressure. The product contained
- 25 30.9% by weight solids and had a Gardner viscosity of <J at 25° C. The product was stable to storage at 25±2° C. for at least 35 days. It was evaluated in paper as described in Example 7. Results are listed in
- 30 Table II.

EXAMPLE 9

- A polyamide prepared according to the procedure outlined in Example 7 was converted to a useful wet-strength resin for
- 35 paper as follows:

- To a solution of 63.0 g. (dry basis) of polyamide in 210.0 g. of water heated to 50° C. was added with stirring 31.0 g. of epichlorohydrin over a period of 3 minutes.
- 40 The temperature of the solution was raised to 70° C. After 23 minutes at 70° C. 17.0 g. of dimethyl sulfate was added during a period of 5 minutes. The solution was heated with stirring at 70° C. until its viscosity at
- 45 25° C. reached >C on the Gardner scale (36 minutes). It was cooled to 25° C. and adjusted to pH 4.0 with 7.5 ml. of 10% by weight sulfuric acid. The product contained 26.6% by weight solids and had a
- 50 Gardner viscosity of >D at 25° C. The product was stable to storage at 25±2° C. for at least 30 days. It was evaluated in paper as described in Example 7. Results are listed in Table II.

EXAMPLE 10

- A polyamide prepared according to the procedure outlined in Example 7 was converted to a useful wet-strength resin for
- 60 paper as follows:

- To a solution of 189.0 g. (dry basis) of the polyamide in 630.0 g. of water heated to 50° C. was added with stirring 75.0 g. of epichlorohydrin over a period of 6 minutes. The temperature of the solution was raised
- 65 to 70° C. and 51.0 g. of dimethyl sulfate

was immediately added over a period of 6 minutes. The solution was heated with stirring at 70° C. until its viscosity at 25° C. on the Gardner scale reached <C (4 hours and 59 minutes). It was cooled to 25° C. and adjusted to pH 4.0 with 7.0 ml. of 10% by weight sulfuric acid. The product contained 25.8% by weight solids and had a Gardner viscosity of <C at 25° C. The product was stable to storage at 25±2° C. for at least 85 days. It was evaluated in paper as described in Example 7. The results are listed in Table II.

EXAMPLE 11

A polyamide prepared according to the procedure outlined in Example 7 was converted to a useful wet-strength resin for

80 paper as follows:

To a solution of 63.0 g. (dry basis) of the polyamide in 100.0 g. of water heated to 50° C. was added with stirring 34.0 g. of epichlorohydrin over a period of 2 minutes. The temperature of the solution was raised to 70° C. and 17.0 g. of dimethyl sulfate was immediately added over a period of 2 minutes. The solution was heated with stirring at 70° C. until its viscosity at 25° C. reached <D on the Gardner scale (1 hour and 12 minutes). It was diluted with 140 g. of water, cooled to 25° C. and adjusted to pH 4.0 with 7.0 ml. of 10% by weight sulfuric acid. The product contained 20.1% by weight solids and had a Gardner viscosity of <A at 25° C. The product was stable to storage at 25±2° C. for at least 85 days. It was evaluated in paper as described in Example 7. The results are listed in Table II.

EXAMPLE 12

A polyamide prepared according to the procedure outlined in Example 7 was converted to a useful wet-strength resin for

105 paper as follows:

To a solution of 31.5 g. (dry basis) of the polyamide in 110 g. of water heated to 50° C. was added with stirring 18.2 g. of epichlorohydrin over a period of 3 minutes. The temperature of the solution was raised to 70° C. and held at this level until the viscosity of the solution reached <D at 25° C. on the Gardner scale (35 minutes). To the solution was added all at once 8.5 g. of dimethyl sulfate. It was then cooled to 25° C. and adjusted to pH 4.0 with 7.0 ml. of 4% by weight hydrochloric acid. The product contained 25.8% by weight solids and had a Gardner viscosity of >B at 25° C. The product was stable to storage at 25±2° C. for at least 90 days. It was evaluated in paper as described in Example 7. The results are listed in Table II.

EXAMPLES 13 AND 14

Cationic polyamide-epichlorohydrin resins were prepared following essentially the procedures of Examples 8 and 12 except that

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the dimethyl sulfate was omitted from the formulations. These resins, which were unstable at solids concentrations of 30.9% by weight and 25.8% by weight, respectively,

were evaluated in paper as described in Example 7. The results are listed in Table II.

TABLE II (1)

Example No.	Per Cent (by weight) Resin Added (Dry Pulp Basis)	Wet Tensile (lb./inch width)	
		Uncured	Cured
7	1.0	6.4	8.8
8	1.0	6.4	11.2
9	1.0	6.5	11.5
10	1.0	6.5	8.7
11	1.0	5.7	9.1
12	1.0	5.1	9.3
13	1.0	6.8	11.5
14	1.0	4.7	9.7

(1) Basis weight of all sheets was 40.0 ± 0.5 lb. per 3000 sq. ft. Waterleaf sheets prepared from the same pulp gave wet tensile results of 0.8 (uncured) and 1.2 (cured) lbs./inch width.

The following examples illustrate the use of other quaternizing agents in the preparation of cationic resins of improved stability in accordance with the invention.

EXAMPLES 15 TO 20

Several samples of a polyamide, prepared according to the procedure outlined in Example 7, were each converted to a useful wet-strength resin as follows:

To 116 g. (63 g. dry basis) of the polyamide solution in a round-bottom flask equipped with mechanical stirrer and thermometer was added 240 g. of water. The solution was heated with stirring to 50° C. and 31 g. of epichlorohydrin was added during a period of 2 minutes. The solution was then heated at 70° C. until the viscosity at 25% by weight solids and 25° C. reached

about A on the Gardner-Holdt scale. The solution was then cooled to a temperature from about 55° C. to about 65° C., the quaternizing agent added, and heating continued within this temperature range until the viscosity at 25% by weight solids and 25° C. was from about >B to <C on the Gardner-Holdt scale. It was then cooled to 25° C. and adjusted to a pH between about 2.0 and 2.5 with concentrated sulfuric acid. The solids concentrations of the products (listed in the order given in Table III below) were 24.5%, 27.0%, 23.5%, 25.2%, 24.3% and 24.7%, all by weight. In all cases, the products were stable to storage at $25 \pm 2^\circ$ C. for at least 90 days. These resins were evaluated in paper as described in Example 7. The results are listed in Table III.

TABLE III ⁽¹⁾

Example No.	Quaternizing Agent — Type	Quaternizing Agent — grams	Per cent (by weight) Resin added (Dry Pulp Basis)	Wet Tensile (lb./inch width)	
				Uncured	Cured
15	methyl iodide	20.9	1%	6.0	11.5
16	diethyl sulfate	22.6	1%	5.1	10.1
17	ethyl bromide	16.0	1%	6.1	10.6
18	1-chloro glycerol	16.2	1%	5.5	10.0
19	1,3-dichloro-glycerol	19.0	1%	5.4	9.5
20	benzyl chloride	18.6	1%	5.3	9.2

⁽¹⁾ Basis weight of all sheets was 40.0 ± 0.5 lb. per 3000 sq. ft. Waterleaf sheets prepared from the same pulp gave wet tensile results of 0.8 (uncured) and 1.2 (cured) lbs./inch width.

EXAMPLE 21

Six hundred fifteen grams of diethylenetriamine and 300 g. of water were placed in a three-necked flask equipped with stirrer, condenser and thermometer. To this was added 870 g. of adipic acid. After the acid had dissolved in the amine, the solution was heated to 180–185° C. for an hour and 15 minutes. The solution was then cooled to 140° under vacuum (approximately 30 mm. of mercury). The vacuum was removed and 1290 g. water was slowly added. The product contained 50.0% solids by weight.

To 260 g. of the above polyamide solution in a round bottom flask was added 150 g. of water. This solution was slowly heated to 50° and 50 g. of epichlorohydrin was added dropwise over a period of ten minutes.

The solution was then heated to 60° for eleven minutes, 6 ml. of concentrated hydrochloric acid was added, and the product was cooled to 25°. Then 25 ml. of concentrated HCl was added to adjust the pH to 5.0.

The solution contained 37.7% solids by weight and had a viscosity of B on the Gardner scale. This condensate solution was stored for 5 weeks and then evaluated in paper as follows:

The solution was adjusted to 20% solids by weight by the addition of water. Sodium carbonate was added to raise the pH to 11. This solution was then allowed to stand at room temperature until its viscosity reached C on the Gardner scale. Sufficient water was then added to lower the solids to 2% by weight and the pH was adjusted to 5 with 10% by weight HCl. This solution was then ready to use as a wet-strength paper resin.

Tacoma bleached kraft pulp was beaten to a Schopper-Reigler freeness of 750 cc. in a Noble and Wood cycle beater. This stock was adjusted to pH 9 with 10% by weight sodium hydroxide and 1% by weight of the above paper resin was added. It was then sheeted on a Noble and Wood handsheet machine using a closed system in which the white water contained 300 p.p.m. of sulfate ion and had been adjusted to pH 9 with 10% by weight sodium hydroxide. The handsheets were dried on a conventional drum drier. A portion of these were given an additional cure of one hour at 105°. The sheets were soaked for two hours in distilled water and tested for wet strength. The results are listed in Table IV.

EXAMPLE 22

Two hundred g of diethylenetriamine and 100 g. of water were placed in a three-necked flask equipped with a take-off condenser, mechanical stirrer and thermometer. To this was added 290 g. of adipic acid. After the acid had dissolved, the solution was heated to 180° C. for 55 minutes. The polyamide was cooled to 140° C. under a vacuum of 30 mm. and 430 ml. of H₂O was added. The product was then cooled to 25° C. analysis of polyamide solution showed the following:

Total Solids - - 50.5% by weight
Acid Number - - 3.3

An epichlorohydrin complex was prepared from the polyamide in the following manner: 258 g. of the above polyamide plus 150 g. of water were weighed into a 500-ml. round-

bottom three-necked flask. To this was added 50 g. of epichlorohydrin at room temperature. This solution was then heated to 60°. It was maintained at 60° for ten minutes and then 10 cc. of concentrated hydrochloric acid was added. The solution was then cooled immediately to room temperature and adjusted to pH 5 with 24 ml. of concentrated hydrochloric acid. The final viscosity of the solution was B on the Gardner scale and it contained 37.4% solids by weight. After storage for 8 weeks at 25° C., this complex was prepared for use in paper by adjusting the solids to 20% by weight, the pH to 11 with sodium hydroxide, and then allowing the solution to stand at room temperature until the viscosity had reached E on the Gardner scale. Sufficient concentrated hydrochloric acid was then added to adjust the pH to 5 and the solids were reduced to 2% by weight, by the addition of water. This solution was then ready for use in paper. This resin solution was evaluated as described under Example 21. Results are listed in Table IV.

EXAMPLE 23

Two hundred twenty-five grams (2.18 moles) of diethylenetriamine and 100 grams of water were placed in a 3-necked flask equipped with a mechanical stirrer, thermo-

meter and condenser. To this was added 290 grams (2.0 moles) of adipic acid. After the acid had dissolved in the amine, the solution was heated to 185–200° C. and held there for 1½ hours. Then vacuum from a water pump was applied to the flask during the period required for the contents of the flask to cool to 140° C. following which 430 grams of H₂O was added. The polyamide solution contained 52.3% solids by weight and had an acid number of 2.1.

To 60 grams of this polyamide solution in a round-bottom flask was added 225 grams of H₂O. This solution was heated to 50° C. and 12.5 grams of epichlorohydrin was added dropwise over a period of 11 minutes. The contents of the flask was then heated to 60–70° C. until it had attained a Gardner viscosity of >E. Then 150 grams of H₂O was added to the product, and it was cooled to 25° C. Eleven ml. of 10% HCl by weight was then added to adjust the pH to 5.0. The product contained 9.0% solids by weight and had a Gardner viscosity of C–D.

The solids content of the aqueous resin solution, prepared as above described, was adjusted to 2% and evaluated as described in Example 21. Results are listed in Table IV.

TABLE IV

Resin Used	% (by weight) Resin Added Based on Dry Pulp	Basis Weight lb./3000 sq. ft.	Wet Tensile lb./in.	Wet Tensile, Cured lb./in.
From Example 21	1.0	40.6	5.7	8.7
From Example 22	1.0	40.6	6.2	9.4
From Example 23	1.0	40.3	6.3	8.6

The following examples (24–41) illustrate the use of cationic polyamide–epichlorohydrin resins of the type herein disclosed for insolubilizing various water soluble polymers. In these examples parts are by weight unless otherwise specified.

EXAMPLES 24 TO 41

In each example, a 2% by weight aqueous solution of a cationic resin, prepared as in Example 1, was mixed with an aqueous solution of the water-soluble polymer, the resulting mixture was adjusted to the desired pH with hydrochloric acid or sodium hydroxide and films of the resulting mixture were cast and dried on a glass plate. Various characteristics of the films were then determined. The results are tabulated in Table V.

Solubility of the film was determined by

measuring the loss in weight of a one-mil thick dried film after immersing 24 hours in water at 73° F. Per cent swell was determined by measuring the increase in length of a one-mil thick dried film after immersing in water at 73° F. for 24 hours and expressing the increase in length of the film as a percentage of the original length. Elongation was determined on a one-mil thick dried film by conventional methods while making standard tensile strength measurements (i.e., elongation employing a load which gives elongation to break). In the examples where the film is reported as insoluble without giving the per cent insoluble, the film retained its shape after the above water-soaking without any appreciable swelling.

In these examples CMC, CMHEC, and CMS mean carboxymethylcellulose, carboxy-

methyl hydroxyethyl cellulose and carboxymethyl starch, respectively, and all are in the form of the water-soluble sodium salt thereof, except as indicated in Example 26 where the water-soluble ammonium salt of CMC is used. Also, in these examples, HEC means hydroxyethyl cellulose and CS means cellulose sulfate. 5

TABLE V

Film Properties

Example No.	Polymer	Resin as % of Polymer	pH of Solution Before Casting	Film Drying	Solubility	% Insoluble	Tensile Strength p.s.i.	% Elongation	Flexibility	% Swell
24	CMC Type 70M ⁽¹⁾	None	7.0	(2)	Soluble	0	8,590	7	Good	—
25	CMC Type 70M ⁽¹⁾	2	8.0	(2)	Partially soluble	62	—	—	Good	—
26	NH ⁺ CMC	20	8.0	(2)	Insoluble	90	—	—	Good	6
27	CMHEC ⁽²⁾	20	7.0	(2)	Insoluble	—	—	—	—	18
28	HEC ⁽⁴⁾	10	8.0	(1)	Insoluble	91	—	—	—	—
29	CS ⁽⁵⁾	20	8.0	(2)	Insoluble	—	—	—	—	—
30	Potato starch	10	5.5	(1)	Insoluble	96	—	—	—	—
31	Wheat starch	10	8.0	(2)	Insoluble	90	—	—	—	—
32	CMS ⁽⁶⁾	20	9.0	(2)	Insoluble	90	—	—	—	—
33	Algin	20	6.8	(2)	Insoluble	92	—	—	—	12
34	Locust Bean gum	20	4.7	(2)	Insoluble	88	—	—	—	—
35	Gelatin ⁽⁸⁾	20	7.5	(9)	Insoluble	92	—	—	—	—
36	Poly(vinyl alcohol) ⁽¹⁰⁾	20	7.5	(9)	Partially soluble	70	—	—	—	—
37	Polyacrylic acid ⁽¹¹⁾	20	9.2	(1)	Insoluble	81	—	—	—	—
38	Polyacrylamide ⁽¹²⁾	20	8.0	(1)	Insoluble	85	—	—	—	—
39	CMC Type 70M ⁽¹⁾	5	8.0	(9)	Insoluble	85	—	—	—	—
40	CMC Type 70M ⁽¹⁾	30	8.0	(1)	Insoluble	82	—	—	—	25
41	CMC Type 70M ⁽¹⁾	175	8.5	(13)	Insoluble	83	—	—	—	37.5

(1) Hercules Medium-Viscosity CMC, D.S. 0.89, viscosity 800 cps. at 2%.

(2) 1 hour at 70° C.

(3) D.S. CM 0.36, HE 0.76, Viscosity 780 cps. at 2%.

(4) D.S. 1.6 Viscosity 6800 cps. at 2%.

(5) D.S. 0.31 Viscosity 1000 cps. at 2%.

(6) Carboxymethylated wheat starch. D.S. 0.67.

(7) Viscosity 1180 cps. at 2%.

(8) 0.5 hour at 105° C.

(9) 205 Bloom gelatin.

(9) Substantially to dryness at 65° C. under a vacuum of 30 inches of mercury.

(10) Elvanol type 32-70 by duPont, Wilmington, Del. (77% hydrolyzed).

(11) Acrysol type GS by Rohm & Haas Co., Philadelphia, Pa.

(12) Type 100 by American Cyanamid Co., New York, N.Y.

(13) 24 hours at room temperature.

The following example illustrates the use of the cationic resins of the invention in conjunction with the incorporation of water-soluble, carboxyl-containing materials into paper and the like.

EXAMPLE 42

Weyerhaeuser bleached sulfite softwood pulp was beaten in pH 7 water with a Noble and Wood cycle beater to a Schopper-Reigler freeness of 825 ml. The pulp slurry was diluted to 2.5% by weight consistency with pH 7 water. The following chemicals were added to 2-liter portions of this slurry with stirring.

(1a) A sufficient volume of 10% by weight aluminum sulfate solution to reduce the slurry pH to 4.5.

(1b) 1% (based on dry weight of pulp) of a dry-strength additive consisting of a 90:10 acrylamide—acrylic acid copolymer, added as a 1% by weight aqueous solution. After a few minutes of stirring, sufficient alum solution was added to reduce the slurry pH to 4.5 as in (1a) above. This acrylamide—acrylic acid copolymer was prepared by adding the following materials, in order listed, to a pressure-resistant polymerization bottle:

9.0 g. recrystallized acrylamide
185.0 g. distilled water
1.0 g. distilled acrylic acid
0.5 g. isopropanol
5.0 cc. 1% solution of $K_2S_2O_8$ in distilled water.

Immediately after addition of the catalyst, the contents of the bottle were blanketed with nitrogen for several minutes. The bottle was then capped and evacuated with a water aspirator for one minute. Nitrogen was added to a total pressure of 46 p.s.i., and the bottle was re-evacuated. This flushing and evacuation process was repeated once more, after which nitrogen was added to a total pressure of 30 p.s.i. The polymerization bottle was then placed on a tumbler at 22° C. and rotated for several days. The viscous solution which resulted was shortstopped with hydroquinone, and a total solids determination showed that complete conversion to a polymeric product had been obtained. The solution was diluted to a concentration of 1% by weight (specific viscosity=150), and its pH was adjusted to 8.2 with NaOH. It was then stored at 1° C. until use.

(1c) 1% (based on dry weight of pulp) of a polyamide—epichlorohydrin condensation

product as an aqueous solution. The condensation product was prepared by the following procedure: To a mixture of 1914 g. of triethylene tetramine and 600 g. of water, 1740 g. of adipic acid was added in several portions, allowing one portion to dissolve before the next was added. The resulting mixture was heated to 195–200° C. for 1½ hours, and water was distilled off continuously during the entire heating period. The mixture was then cooled to 140° C. under vacuum and 3 liters of 80° C. water was then added cautiously. The polyamide product had a total solids content of 54.4% by weight and an acid number of 3.6. Water was used to dilute 2162 g. of this product to a total weight of 10,751 g. The aqueous solution was stirred and heated to 45° C. At this stage, the addition of 1025 g. of epichlorohydrin was started. The addition was complete by the time the temperature reached 60° C. The mixture was then held between 60° and 70° C. until its Gardner-Holdt viscosity reached a value of E. Then 9 liters of water and 250 ml. of 3.7% by weight HCl solution were added. The final product had a pH of 5.75 and a total solids content of 11.0% by weight.

(1d) 1% by weight of the polyamide—epichlorohydrin condensation product described in (1c) above (based on dry weight of pulp). After a few minutes of stirring, an equal weight of the acrylamide—acrylic acid copolymer described in (1b) above was added to the slurry. The final slurry pH value for both (1c) and (1d) was about 7.0.

All slurry samples were diluted to 0.25% by weight consistency with pH 7 water and then diluted further to a deckle box consistency of 0.025% by weight in order to form 40-pound basis weight (24×36—500 sheet ream) handsheets, using a Noble and Wood sheetmaking apparatus. A closed white water system was employed. Formed sheets were wet pressed to 35–40% by weight solids content and then dried at 250° F. on a steam drum drier. After conditioning for several days at 73° F. and 50% relative humidity, the sheets were tested in the same environment for various paper strength properties, using standard testing equipment. Strength data were corrected to 40 pounds/ream basis weight by use of the linear relation $S=kB$, where S represents the strength property and B represents sheet basis weight. The results are set forth in Table VI.

TABLE VI

Experiment	Dry Strength Properties (Corrected to 40 lb./R. basis wt.)		% Increase in Tear-Burst Sheet Strength of Control ¹	Uncured Wet Tensile Strength (after 2-hour soak in distilled water)
	Elmendorf Tear (g./sheet)	Mullen Burst (p.s.i.)		
1a	86	20	Control	not tested
1b	60	35	16.4	1.6 lb./in.
1c	74	25	4.5	3.4
1d	54	39	20.0	6.3

¹ TAPPI 40, p. 499, July, 1957.

The above data show that when a cationic polyamide—epichlorohydrin resin of the type herein disclosed is used with the acrylic copolymer dry strength additive, there is an improvement in overall tear-burst sheet strength of 20%, as compared with the alumed control, whereas the resin alone produced an improvement of 4.5% and the alum plus dry strength additive produced an improvement of 16.4%. Moreover, not only does the polyamide—epichlorohydrin resin produce wet strength, while the alum treatment does not, but the combination of the acrylic copolymer with the resin shows a synergistic effect which almost doubles the wet tensile strength produced by the resin alone. Thus the dry strength additive and the resin mutually enhance the separate effects of each.

The following examples (43—46) illustrate the use of the cationic resins of the invention in conjunction with the incorporation of water-insoluble coating, impregnating and sizing materials into paper.

EXAMPLE 43

A ketene dimer composition was made up in the following manner. Into a Waring blender was placed 10 parts of "Hi-Sil 303," a purified low-density silica manufactured by Columbia-Southern Chemical Division of the Pittsburgh Plate Glass Company. The blender vessel was warmed in a steam bath to about 50° C. and 10 parts of molten alkylketene dimer prepared from a mixture of myristic and palmitic acids (m.p. ca. 33° C.) was added dropwise to the vigorously-agitated silica. The product was removed from the blender in the form of a free-

flowing powder made up of ketene dimer supported on silica in a weight ratio of 1:1.

A 1% by weight aqueous slurry of the ketene dimer composition, prepared as above described, was made using mild beating in a Waring blender. Several portions of this slurry were each beaten 3 minutes in a Waring blender with 500 ml. of 2.5% by weight consistency Weyerhaeuser bleached sulfite pulp which had been previously beaten to 750 Schopper-Reigler freeness in pH 8 tap water with the Valley beater. The pulp-slurry mixture in each case was diluted to 5 liters (0.25% by weight consistency) with pH 8 tap water and then varying amounts of a 1% by weight solids solution of various retention aids were added and mixed. For each sheet 450 ml. of each pulp-slurry mixture was diluted to 1.1 liter (0.1% by weight consistency) for sheet formation on a 100-mesh stainless steel screen in a 6½ inch diameter circular sheet mold. Sheets were pressed between felts and dried 60 sec. on a steam heated drum drier at 240° F. Five sheets were made with each pulp-slurry mixture. For the first sheet, tap water was used for dilution to 0.1% consistency. For the remaining sheets white water was used for dilution. Sheets made in this way had a basis weight of about 40 lb./3000 sq. ft. Sizing in the sheets was measured with the Hercules photometer using 20% by weight lactic acid ink after the sheets had aged 48 hours at room temperature. The results in Table VII below are average times (5 sheets tested in each set) to 85% of original reflectance.

TABLE VII

Retention Aid %	Ketene Dimer Composition %	Photometer Sizing Results Seconds	
		Retention Cato 8	Aid — Type Epichlorohydrin- Polyamide Resin
0.5%	0.6%	445	+1000 ¹ 91.8%
0.25%	0.6%	960	+1000 ¹ 90%
0.125%	0.6%	535	1185
0.5%	0.3%	180	775
0.25%	0.3%	95	725
0.125%	0.3%	75	490

¹ At 1000 seconds the reflectance was still over 85% of the original and equal to the percent indicated.

- The epichlorohydrin—polyamide resin utilized in Example 43 was prepared as follows: To 319 g. triethylenetetramine and 100 g. water heated to 123° C. was added 290 g. adipic acid in small portions. When the addition of acid was complete, the mixture was heated to about 190° C. and held at 190—205° C. for about 105 min. At the end of this time, the heat was removed and the pressure over the resin reduced as low as possible without excessive foaming for a period of 10 minutes. Then 500 ml. water was added to give a fluid solution with 49.8% by weight total solids. Sixty-three grams of this solution was diluted with 225 ml. water and heated to 50° C. Heat was removed and the addition of 22 g. epichlorohydrin was started and maintained at a rate which held the temperature of the solution at about 55° C. The addition required 3 minutes. The mixture was warmed to about 60° C. and held at about 60—66° C. for 70 minutes during which time the viscosity of the solution rose to E. At this point 225 ml. water was added and the pH adjusted to 5 with hydrochloric acid. Final viscosity was about C and total solids was 8—9.5%.
- The Cato 8 starch utilized in Example 43 is a cationic starch (modified cornstarch having a nitrogen content of about 0.25%) produced and sold by National Starch Pro-

ducts Company.

EXAMPLE 44

The method of Example 43 was used with the following changes:

1. St. Mary's unbleached kraft pulp pre-beaten to 750 Schopper-Reigler freeness was used.
2. Five ml. of a 0.15% by weight aqueous alkylketene dimer emulsion (0.5% by weight alkylketene dimer based upon dry pulp) was added to each portion of pulp after dilution to 0.25% by weight consistency. The aqueous ketene dimer emulsion was prepared from a blend of 5 parts of an alkylketene dimer prepared from a blend of palmitic and stearic acids and 1 part Atlox 2495, a commercial product of the Atlas Powder Company. Atlox 2495 is the hexaoleate of a sorbitol-ethylene oxide adduct.
3. After 2—3 minutes' mild stirring, varying amounts (10 ml., 5 ml., 2.5 ml. and 1.25 ml. which are 1%, $\frac{1}{2}$ %, $\frac{1}{4}$ % and $\frac{1}{8}$ %, respectively, resin based upon dry pulp) of a 1.25%-solids solution of the epichlorohydrine — polyamide resin of Example 43 were added.

The results of the photometer sizing test with 20% lactic acid ink and the Mullen wet bursts after 24 hours' soaking in water are shown in Table VIII below.

TABLE VIII

Epichlorohydrin-Polyamide Resin % (by weight)	Photometer Time	Mullen Wet Burst
1%	140 sec.	16.0 p.s.i.
0.5%	196 sec.	11.2 p.s.i.
0.25%	3 sec.	7.0 p.s.i.
0.125%	0 sec.	4.0 p.s.i.

The average Mullen wet bursts of similar paper made without the epichlorohydrin-polyamide resin was 3.2 p.s.i.

- 5 **EXAMPLE 45**
 The method of Example 44 was used except that 5 ml of a 1.25% by weight solids wax emulsion was substituted for the 5 ml. of the 0.15% by weight alkylketene emulsion. This is 0.4% by weight wax emul-

sion solids based on dry pulp. The wax emulsion was a commercial product of Hercules Powder Company containing 45% by weight total solids and 43.4% by weight fully refined paraffin wax and known as Paracol 404R.

The results of the photometer sizing test with 20% by weight lactic acid ink and of the Mullen wet burst test after 24-hour soaking are shown in Table IX below.

TABLE IX

Epichlorohydrin-Polyamide Resin	Photometer Time	Mullen Wet Burst
1%	25 sec.	12.3
0.5%	29 sec.	11.2
0.25%	11 sec.	6.4
0.125%	3 sec.	4.1

The average Mullen wet bursts of similar paper made without the epichlorohydrin-polyamide resin was 3.2 p.s.i.

- 25 **EXAMPLE 46**
 McNamee clay (1.25 g.) was added to 5 liters of a 0.25% consistency Tacoma bleached kraft pulp. This pulp had been beaten at ~5% consistency in pH 8 tap water to 750 Schopper-Reigler freeness. This pulp was diluted to 0.25% with pH 8 tap water. After thoroughly mixing the pulp and clay 25 ml. of a 0.125% by weight epichlorohydrin-polyamide resin prepared as in Example 43 was added. This is 0.25% by weight resin based upon the dry pulp. Five sheets were made as in Example 43. A similar set of

five sheets was made without the resin. The white water for each set was filtered through separate filter papers which had been weighed after conditioning 24 hours in a constant - temperature, constant - humidity room. The filter papers with the white water fines were dried, conditioned, and weighed again to measure the weight of fines collected. The weight of the fines divided by the weight of the fines plus the weight of the sheets in each set multiplied by 100 gives the per cent of the pulp and clay used for five sheets which passed the papermaking screen. The ash content of the first, third and fifth sheets in each set was determined. The results are set forth in Table X below.

TABLE X

Retention Aid	% (by weight) Fines Passing Screen	% Ash		
		1st Sheet	3rd Sheet	5th Sheet
0.25% epichlorohydrin-polyamide resin	7.70	3.4	4.0	4.1
None	9.72	1.2	1.5	1.6

5 The following examples (47—49) illustrate the utility of the cationic resins of the invention in connection with the preparation of fibrous sheets and mats from mineral fibers.

EXAMPLE 47

10 Four grams of asbestos fiber was mixed in a Waring blender for 2 minutes with 600 ml. of water. To this was added 80 grams of an 0.1% by weight aqueous solution of the resin, prepared as in Example 1 (2% resin based on dry fiber weight). The slurry

was stirred for 2 minutes and then formed into a mat by means of a handsheet mold. The mat was pressed and drum dried. Other asbestos fiber sheets were formed as above except that the resin was omitted. The sheets were soaked for 30 minutes in distilled water after which they were removed from the water, blotted to remove excess water and then tested for wet strength with a Mullen Burst Tester. Results are given in Table XI below.

TABLE XI

% Resin Added Based on Dry Fiber Weight	Wet Strength (Mullen) lb./sq. in.
2	5.1
0	Nil (sheets could not even be removed from water in which they were soaked)

EXAMPLE 48

30 Handsheets were prepared from asbestos fiber by stirring 4.0 grams of fiber with 600 ml. of water for 2 minutes in a Waring blender. Then an 0.1% by weight aqueous solution of the resin, prepared as in Example 1, was added and the pulp slurry was stirred for an additional 5 minutes. The hand-

sheets were formed on a circular 6-inch sheet mold, pressed and drum dried. The dry sheets were given an additional cure of 1 hour in an oven at 105° C. They were then soaked in distilled water for 30 minutes and tested for wet strength using a Mullen Burst Tester. Results are given in Table XII below.

TABLE XII

% Resin Added Based on Dry Fiber Weight	Wet Strength (Mullen) lb./sq. in.
2	4.4
2	4.5
4	5.6
4	5.0
0	0*
0	0*

* These sheets could not be removed from water without disintegrating.

EXAMPLE 49

Handsheets were prepared from a blend of 75% by weight glass fiber and 25% by weight Tacoma bleached kraft pulp. They were formed in a circular sheet mold 6 inches in diameter. A slurry was made of 2.25 grams of glass fiber plus 0.75 grams of Tacoma bleached kraft pulp in 300 ml. of water. This was stirred for 2 minutes in a Waring blendor. The pH was adjusted to 9.5 with 10% by weight NaOH and 360 grams of

an 0.1% by weight solution of the resin, prepared as in Example 1 (12% solids based on weight of dry fiber), was added. After stirring for 2 minutes, the slurry was formed into a sheet, pressed and drum dried. A similar sheet was prepared except that no resin was added. Both sheets were soaked for 30 minutes in distilled water and then tested with a Mullen Burst Tester for wet strength. Results are given in Table XIII below.

TABLE XIII

% Resin Added Based on Dry Fiber Weight	Wet Burst lb./sq. in.
12	5.0
0	(too weak to test)

The following examples (50—53) illustrate the application of the cationic resins of the invention in preventing shrinkage and felting of wool.

EXAMPLE 50

A sample of scoured, carbonized and bleached wool flannel cloth was treated in the following manner with a 5% by weight aqueous solution of the cationic thermosetting resin prepared as in Example 1. The dry fabric was padded, double ends, through a room-temperature solution of the resin on a 10-inch laboratory padder. The wet pick-up was found to be 113% by weight (5.6% resin solids based on the dry weight of the cloth). The treated fabric was air-dried and cured for 5 minutes at 150° C. after which

it was washed for 45 minutes in a 130° F., 0.1% by weight neutral soap wash. After air-drying, the total shrinkage of the fabric was 9.1%. This compared to 50% shrinkage for an untreated sample. It should be noted that these values represent total shrinkage, i.e., relaxation shrinkage plus felting shrinkage. The hand and color of the fabric after washing were not impaired by the foregoing treatment.

EXAMPLE 51

The treated sample from Example 50 was given a second wash as described in Example 50, followed by $\frac{1}{2}$ -hour room temperature dry-cleaning cycle, followed by a third wash cycle. The additional shrinkage after these treatments was found to be nil.

EXAMPLE 52

A sample of woolen fabric was treated as in Example 50 with a 5.1% by weight aqueous solution of the cationic resin prepared as in Example 1 and cured for 5 minutes at 100° C. The wet pick-up was 100% by weight (5.1% resin solids based on dry weight of the fabric). It was washed and dried as previously described. The total shrinkage was found to be 6.1%.

EXAMPLE 53

A sample of woolen fabric was treated with a 3.13% by weight aqueous solution of the cationic resin prepared as described above and treated as in Example 52. The wet pick-up was 100% by weight (3.13% resin solids based on dry weight of the fabric). After washing, its total shrinkage was 3.1%. This sample was given four additional launderings. The increased shrinkage due to the extended laundering was 4.8%, or a total of 7.9% after five launderings.

The following examples (54—59) will illustrate the application of the cationic resins of the invention in the preparation of nonwoven fabrics.

EXAMPLE 54

A web of 15 denier 1-9/16-inch staple, bright, crimped rayon fibers was saturated a 10% by weight solution of the resin, prepared as in Example 1, and padded through a laboratory Butterworth padder to a dry resin pick-up of 7.4% by weight. The fabric was dried and cured at 100° C. for 5 minutes. The wet and dry tensile strength of the cured fabric was measured on an Instron testing machine at a crosshead speed of 12 in./min. The data were reported as maximum load in pounds to break an inch-wide strip rather than the usual pounds per square inch, due to the uneven surface characteristics of the fabric. The foregoing resin-treated fabric had a dry break of $0.17 \pm .04$ pounds, and a wet break of $0.09 \pm .01$ pounds.

EXAMPLES 55 TO 57

Two samples of the same type of nonwoven fabric web were treated with a poly(vinyl acetate) latex (du Pont Elvacet 81—900) as in Example 54, and a third with a combination of polyamide—epichlorhydrin resin (prepared as in Example 1) and the latex. The properties of the resultant fabrics are described in Table XIV below.

TABLE XIV

Ex.	Binder (% by dry weight on fabric)	Maximum load to break (lb.)	
		Dry	Wet
55	7.86% Poly(vinyl acetate)	$0.13 \pm .04$	$0.05 \pm .01$
56	16.91% Poly(vinyl acetate)	$0.30 \pm .01$	0.04 ± 0
57	{ 10.28% Poly(vinyl acetate) 5.14% resin }	$0.4 \pm .02$	$0.09 \pm .02$

EXAMPLES 58 AND 59

Webs of 3 denier, 2-inch staple bright, regular rayon fiber was treated with a polyacrylic latex (Rohm and Haas' AC-33, believed to be approximately a 70:30 copolymer of ethyl acrylate and methyl meth-

acrylate) as in Example 54, and with a combination of this latex and polyamide—epichlorohydrin resin (prepared as in Example 1). The properties of the resultant fabrics are described in Table XV below.

TABLE XV

Ex.	Binder (% by dry weight on fabric)	Maximum load to break (lb.)	
		Dry	Wet
58	17.2% Polyacrylate	7 ± 2	$0.7 \pm .2$
59	{ 19.7% Polyacrylate 3.9 % Resin }	13 ± 4	5 ± 1

The following examples (60 and 61) illustrate the application of the cationic resins of the invention in the treatment of nonfibrous regenerated cellulose film to improve the bonding of said film to the subsequently applied top coat.

EXAMPLE 60

Following the procedure of Example 1, a cationic resin was prepared utilizing 0.97 moles of diethylene triamine, 1.0 mole of adipic acid and sufficient epichlorohydrin to give a ratio of 1.15 moles of epichlorohydrin to 1 mole of secondary amine in the polyamide formed from the diethylene triamine and the adipic acid. An aqueous solution of this resin containing 9.6% by weight solids was applied to plasticized Cellophane (Registered Trade Mark) by means of conventional spray equipment and dried in a forced draft oven at 90° C. After 15 minutes' drying time, the film was unwrinkled, non-tacky, nonblocking, transparent and lustrous. Spraying was done to both sides in such a way that a film thickness of 0.1 mils (0.0001 inches) of dried coating was obtained.

The film was subsequently sprayed with a nitrocellulose-based coating similar to that described in United States Patent Specification No. 2,236,546, and dried for 30 minutes at 66° C. A film thus prepared was immersed in water. Similarly, a film with no anchor coating, but bearing the nitrocellulose coating, was immersed in water. The film bearing both the cationic resin-anchor coat, and nitrocellulose coat, remained unchanged after four weeks' immersion, whereas the film to which no anchor coat and a nitrocellulose lacquer had been applied blushed badly after only 1 hour. The tensile properties of the resin-coated film were the same as those of an uncoated, plasticized cellophane.

EXAMPLE 61

A plasticized, untreated Cellophane film was dip coated in a 9.6% by weight solids water solution of the cationic resin, prepared as above described, for 2 minutes, allowed to drain and the film then heated for 2 hours under a pressure of 10 mm. of Hg at 65° C. Films which had been so treated and subsequently sprayed with a protective moisture-resistant nitrocellulose lacquer coating and dried, as in Example 60, possessed a moisture vapour transmission rate of 4.2—4.9 g./24 hrs./sq.m., whereas films which had received no anchor coating but had received a spray coating of nitrocellulose lacquer, possessed a moisture vapor transmission of 6—8 g./24 hrs./sq.m.

It will thus be seen that the present invention provides novel cationic water-soluble thermosetting resins or water-soluble condensates which may be converted readily to cationic resins by further condensation. These resins may be used under acid, neutral or alkaline conditions in a variety of applications

as will be evident from the above description and examples.

WHAT WE CLAIM IS:—

1. A process of preparing water-soluble condensates which comprises forming a water-soluble polyamide by heating together at reaction temperatures a C_3 to C_{10} saturated aliphatic dibasic carboxylic acid and a polyalkylene polyamine containing 2—8 alkylene groups, and then reacting the polyamide with epichlorohydrin.

2. A process according to claim 1 in which the reaction of the polyamide with the epichlorohydrin is terminated before any substantial cross-linking takes place to form a water-soluble condensate which may be converted readily to a water-soluble cationic resin by further condensation.

3. A process according to claim 1 in which the reaction of the polyamide with the epichlorohydrin is continued until a water-soluble cationic thermosetting resin is produced.

4. A process according to claim 3 in which a quaternizing agent is included in the polyamide—epichlorohydrin reaction mixture and reacted therewith to improve the stability of the cationic resin.

5. A process according to claim 4 in which the quaternizing agent is a compound having an alkyl group or substituted alkyl group which is readily available for alkylation.

6. A process according to claim 5 in which the quaternizing agent is dimethyl sulfate.

7. A process according to claim 1 in which the mole ratio of polyalkylene polyamine to dibasic carboxylic acid is from 0.8:1 to 1.4:1 and the reaction between the polyalkylene polyamine and the dibasic carboxylic acid is carried out at a temperature from 160° C. to 210° C.

8. A process according to claim 7 in which the mole ratio of epichlorohydrin to secondary amine groups of the polyamide is from 0.5:1 to 1.8:1 and the reaction of the epichlorohydrin with the polyamide is carried out at a temperature from 45° C. to 100° C.

9. A process according to claim 8 in which a quaternizing agent is included in the polyamide—epichlorohydrin reaction mixture in an amount sufficient to convert from 25% to 75% of the tertiary amine groups to quaternary groups.

10. A water-soluble polyamide—epichlorohydrin condensate produced in accordance with any of the preceding claims.

11. A water-soluble cationic thermosetting resin produced in accordance with any of the preceding claims.

12. A water-soluble cationic thermosetting resin produced substantially as described in any of the examples.

13. Process of producing paper and paper

- products having improved wet-strength from fibrous cellulosic material which comprises applying to the fibers thereof an aqueous solution of the resin claimed in claim 11 or claim 12.
14. Process according to claim 13 in which the amount of resin adsorbed by the fibers is from about 0.1% to 5% by weight of the fibers.
15. A process for the production of wet-strength paper which comprises adding the resin claimed in claims 11 or 12 to an aqueous suspension of cellulosic paper stock, forming the stock so treated into a sheet, and drying the sheet.
16. Wet strength paper prepared by the process claimed in any of claims 13 to 15.
17. Process of preparing a substantially water-insoluble product which comprises forming an aqueous solution of a water-soluble polymer as hereinafter defined and the resin claimed in claims 11 or 12, and drying the resulting aqueous solution.
18. The process of claim 17 wherein the water-soluble polymer is a cellulose derivative.
19. The process of claim 17 wherein the water-soluble polymer is selected from starch and starch derivatives.
20. The process of claim 17 wherein the water-soluble polymer is carboxymethyl-cellulose.
21. Products prepared by the process claimed in any of claims 17 to 20.
22. A process for treating fibrous cellulosic material with a water-soluble, carboxyl-containing compound as herein defined which process comprises forming an aqueous suspension of the fibrous material, adding to and mixing with said aqueous suspension from 0.1% to 5%, based on the dry weight of fibers, of the resin claimed in claims 11 or 12, and then adding to said aqueous suspension from 0.25% to 10%, based on the dry weight of fibers, of a water-soluble carboxyl-containing compound, whereby a substantial portion of said water-soluble carboxyl containing compound is deposited on and attached to said fibrous material together with said resin.
23. Process according to claim 22 where the water-soluble carboxyl-containing compound is selected from the group consisting of polymers and copolymers of acrylic acid, polymers and copolymers of methacrylic acid, condensates of lower alkylene oxides with polymers and copolymers of acrylic acid, methacrylic acid and itaconic acid, water-dispersible alkali metal salts of rosin, alkali metal salts of C_{10} — C_{22} fatty acids, carboxyl-containing cellulose derivatives and copolymers of maleic anhydride.
24. The product prepared by the process of claims 22 or 23.
25. In a process of making a formed cellulosic product by the steps of preparing an aqueous suspension of fibrous cellulosic material, adding thereto a water-insoluble coating, impregnating and/or sizing agent, and forming the thus-treated cellulosic material into a felted product, the improvement comprising incorporating in said aqueous suspension of fibrous cellulosic material along with said water-insoluble coating, impregnating and/or sizing agent, from 0.1% to 5%, based on the dry weight of fibers, of the resin claimed in claims 11 or 12, whereby a substantial portion of said water-insoluble coating, impregnating and/or sizing agent is deposited on and attached to said fibrous material together with said resin.
26. A process according to claim 25 wherein the water-insoluble coating, impregnating and/or sizing material is selected from the group consisting of alkylketene dimers, resins, waxes and latices.
27. The product prepared by the process of claims 25 or 26.
28. Process of preparing a mineral fiber product having improved wet-strength which comprises adding an aqueous solution of the resin claimed in claims 11 or 12 to an aqueous suspension of mineral fibers, adsorbing from 0.4% to 12%, based on the weight of fiber, of said resin on said mineral fiber, forming the thus treated fiber into a sheet, and drying the sheet.
29. A mineral fiber product prepared by the process claimed in claim 28.
30. A process of treating wool fabrics to prevent shrinkage thereof during washing which comprises treating the fabric with an aqueous solution containing at least 0.5% by weight, based on the weight of fabric, of the resin claimed in claims 11 or 12, and then drying the fabric.
31. A wool fabric having improved resistance to shrinkage prepared by the process of claim 30.
32. The process of preparing a nonwoven fabric having improved strength which comprises forming textile fibers into a web, applying to the web an aqueous solution of the resin claimed in claims 11 or 12, and drying the web.
33. The process of claim 31 wherein the aqueous solution of the resin is applied to the web in conjunction with a latex emulsion.
34. A nonwoven fabric prepared by the process of claims 32 or 33.
35. A process for treating nonfibrous regenerated cellulose film to improve the anchorage of said films to a subsequently applied top coat which comprises treating

said film with an aqueous solution of the resin claimed in claims 11 or 12, drying the film, and applying thereto a water-repellent top coat.

- 5 36. A nonfibrous regenerated cellulose film prepared by the process of claim 35.

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Patent Division

ERRATA

865,727

SPECIFICATION No. 865,727

Page 5, line 10, for "in" read "to"
Page 5, line 127, for "are" read "art"
Page 7, line 39, for "ketone" read "ketene"
Page 8, line 69, for "later" read "latter"
Page 9, line 3, for "NaO" read "NaOH"
Page 9, line 24, for "epichloro-" read
"epichlorohydrin"
Page 9, line 64, for "azelic" read "azelaic"
Page 10, line 86, for "heated" read "sheeted"
Page 12, line 41, for "in" read "In"
Page 13, line 69, for "analysis" read
"Analysis"
Page 17, line 39, for "46" read "45"
Page 23, line 29, after "saturated" insert
"with"

THE PATENT OFFICE

3rd July 1961